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Development of Lithium Diffused Radiation Resistant Solar Cells

Report No. 6

Second Quarterly Report

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SUMMARY

Boron diffusion studies were performed. A process was successfully developed using a BBr_3 source. Good output was achieved and stresses were negligible as demonstrated by diffusing 2x6 cm size blanks that were only 0.006 inch thick.

Humidity exposure tests showed that the solderless Ti-Ag contact on P/N cells is not humidity resistant.

Cells made using an eight-hour lithium diffusion at 325°C have had very good efficiencies. In fact, the distribution curve of the 60 cells sent to JPL as Lot 3 with these diffusion parameters showed that these cells had the highest efficiencies of any fabricated to date.

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1.0 INTRODUCTION

The goal of this contract is to investigate the effect of various process parameters on lithium doped solar cell performance. This program is a continuation of work done on JPL contract 952247, and it has been organized into five areas of study. The five basic areas include: P-N diffusion studies, material studies, lithium diffusion studies, special structure studies and contact studies.

The purpose of the P-N diffusion studies is to develop a boron diffusion which: 1) does not etch silicon, 2) will yield higher efficiency lithium cells due to reduced stresses and 3) can be used for larger area and thinner cells (also due to reduced stresses).

As part of the material studies parameters such as oxygen content, crystal growth rate and blank thickness will be investigated.

The lithium diffusion studies will be directed toward improving cell efficiency and obtaining maximum radiation damage recovery. Radiation studies conducted under JPL contract by other laboratories during the past year have shown in one limited experiment that long lithium diffusions done around 325°C result in higher efficiency and more radiation resistant lithium cells. These diffusion parameters as well as the process techniques of complete lithium coverage of the back cell surface and lithium evaporations were used in fabricating the cells that showed unusually good radiation recovery, so these same parameters will be further investigated in this program in order to determine if these results can be reproduced.

The contact studies will include evaluation of the Ti-Ag contacts presently used as well as investigation of other contact metals such as Pd and Al.

The special structures to be studied will be lithium cells with integral covers and a lithium cell with a high concentration N+ region at the junction.

In addition to the experimental studies, 600 lithium doped solar cells will be fabricated for radiation testing and analysis by JPL.

During this quarter, boron diffusion sources and eight-hour lithium diffusions at 325°C were areas investigated. The Ti-Ag contacts were evaluated for strength and humidity resistance.

2.0 TECHNICAL DISCUSSION

2.1 BORON DIFFUSION STUDIES

During this quarter the boron diffusion system described in the previous quarterly report was further optimized using a BBr_3 source and an oxidizing carrier gas ambient. The variables studied during this period included: 1) impurity flow density along the diffusion zone, 2) carrier gas flow rates, and 3) diffusion time. All of the above were evaluated in respect to overall cell performance, uniformity of the deposited glass layer, uniformity of p-type conversion, and finally the diffused-layer sheet resistivity.

Non-uniform impurity flow along the diffusion zone due to source (BBr_3) depletion was reported in the last quarter, but was rectified with a modification in the flow pattern. This flow pattern was altered by providing connections for the incoming and exhausting gases at the front of the system with the rear of the diffusion tube closed. An experiment was then conducted in which a matrix of flow rates for the carrier and impurity gases was designed and diffusions were performed. The evaluation of this experiment was based on the sheet resistivity measurements of the diffused cell blanks.

With these parameters satisfactorily controlled, various diffusions were then performed for different time intervals and the diffused cell blanks were processed into completed solar cells by standard fabrication methods.

The diffusion times producing the more desirable results were 10 and 85 minutes in length. Figures 1 and 2 are the I-V curves taken in a tungsten light source (100 mW/cm^2) for cells diffused for these two respective time intervals. The 10-minute diffusion time of Figure 1 exhibits a "soft" characteristic, but the values of the I_{sc} and V_{oc} were the highest achieved up to that time for any given diffusion. In the case of the 85-minute diffusion of Figure 2, the curve shape is of interest since it has a good curve factor and most closely approximates the type of characteristic obtained with a typical good P-N junction diffused with $BC\ell_3$ although the I_{sc} and V_{oc} values were not optimum.

Repeat runs and slight process modifications with these particular diffusion parameters still did not produce the desired improvements. The components of the BBr_3 system were scrutinized for an explanation of the short circuit current deficiency and possible sources of contamination were sought without success. Since it appeared that the boron diffusions performed in an oxygen atmosphere always had a deficiency in boron source and the resulting junction characteristics and collection efficiencies were poor, it was decided that a new approach was needed. The approach taken was to eliminate the oxygen but to continue to utilize the BBr_3 source since it appeared to be less reactive with silicon than the standard $BC\ell_3$ source.

In this new diffusion process the BBr_3 vapor itself, rather than the boron oxide (B_2O_3) formed by the reaction of oxygen and BBr_3, becomes the local impurity and reacts directly with

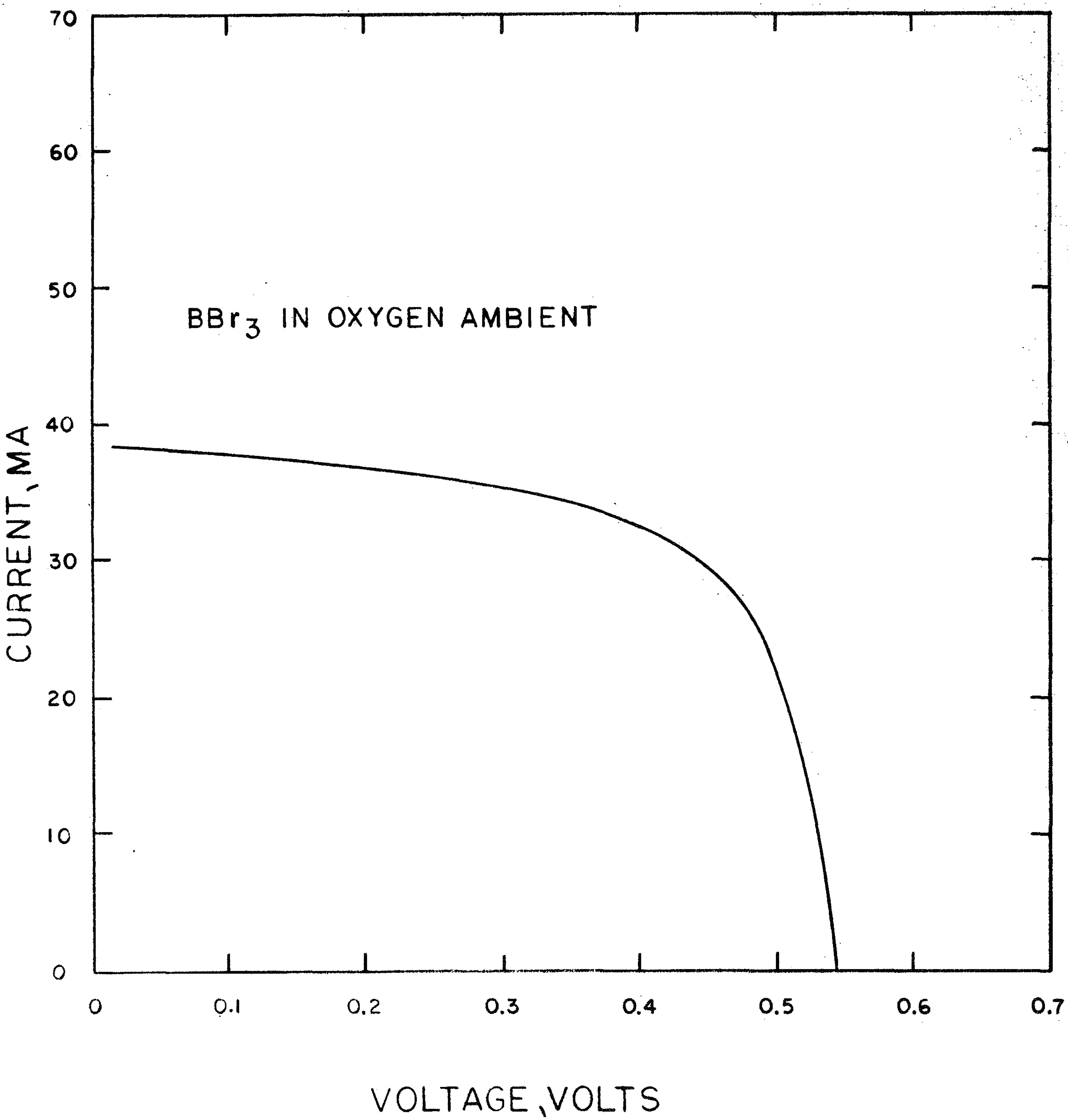

Figure 1. I-V Characteristic of 10 Minute Diffusion Using BBr_3 in an Oxygen Ambient. Tungsten light source - 100 mW/cm^2.

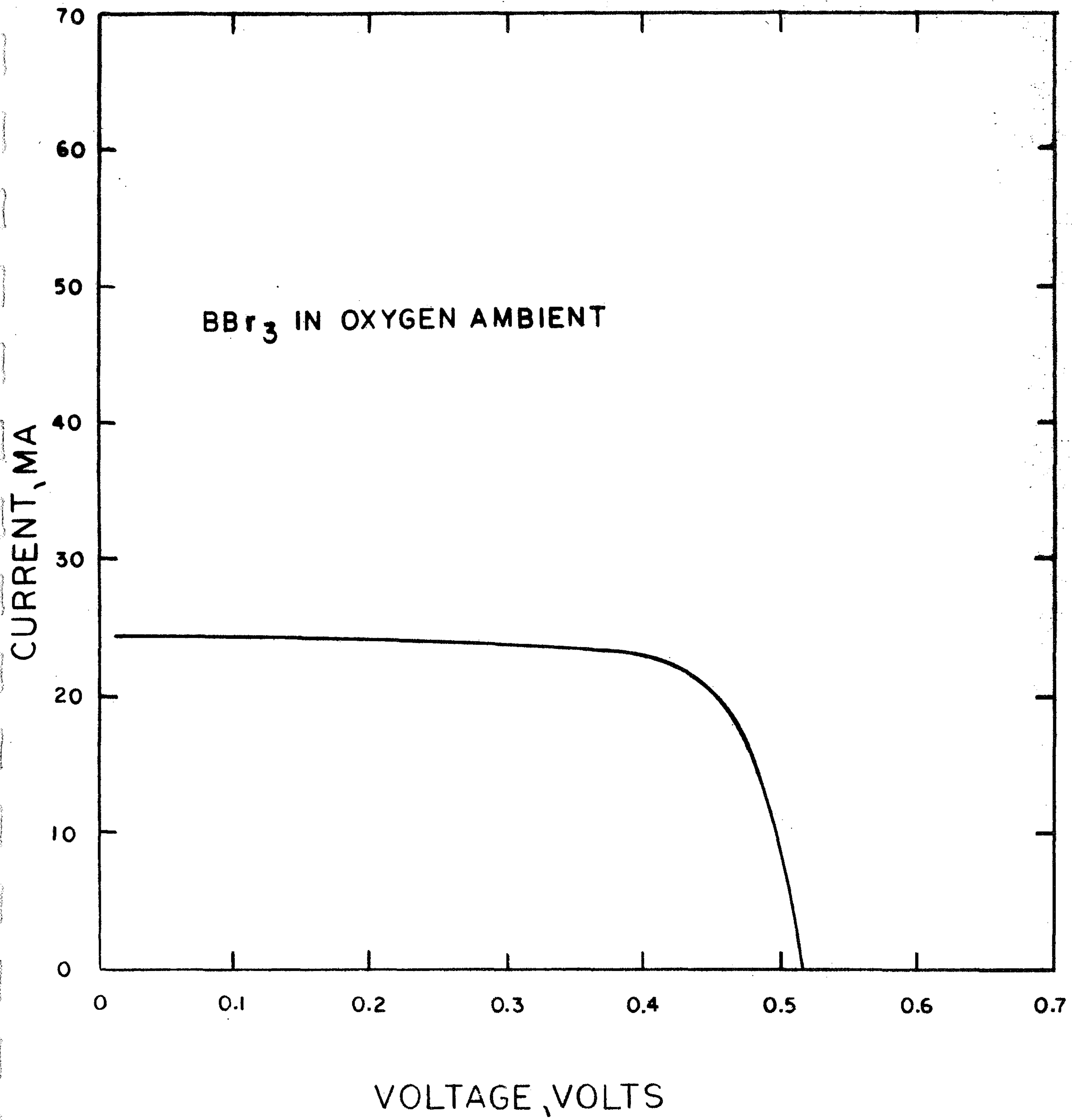

Figure 2. I-V Characteristic of 85 Minute Diffusion Using BBr_3 in an Oxygen Ambient. Tungsten light source - 100 mW/cm^2.

the silicon cell blanks. Silicon is replaced in the reaction and a black boron layer is deposited on the cell surface according to the reaction,

$$4BBr_3 + 3\ Si \rightarrow 3\ SiBr_4 + 4B \qquad \text{Eq. 1}$$

This is essentially the same type of reaction that the standard BCl_3 process produces.

In the case of the BCl_3 process the etching and simultaneous deposition of boron on the cell surface causes a major problem of stressing and often times bowing, especially of large-area cell blanks.

A series of preliminary diffusions was made using BBr_3 in an inert atmosphere to evaluate the stress effects of the process. Both mechanically-lapped and chemically-polished small (1x2 cm) and large (2x2 cm and 2x6 cm) area cell blanks were evaluated. Etching of the cell blanks during diffusion was very slight and there was no evidence of bowing even in the large 2x6 cm blanks. Further tests showed that even if the thickness of the 2x6 cm blanks was reduced to 0.006 inch thickness, there was no noticeable bowing. Exploratory diffusions were then conducted to evaluate the process and determine optimum conditions for meeting sheet resistivity requirements for solar cells. Gas flow patterns were returned to that of the original system with carrier and impurity gases injected in one end and gas exhausting at the other end of the diffusion tube.

With the system operating in this configuration, cell blanks were diffused and P/N solar cells without lithium were fabricated. Figure 3 illustrates the I-V curve in a tungsten light source (100 mW/cm^2) for a cell diffused with BBr_3 in an inert ambient. The cell characteristic indicates that a good P-N junction was obtained and the I_{sc} and V_{oc}, although not quite optimum, were good and exhibit a significant improvement over previous BBr_3 diffused cells. Figure 4 is the I-V characteristic

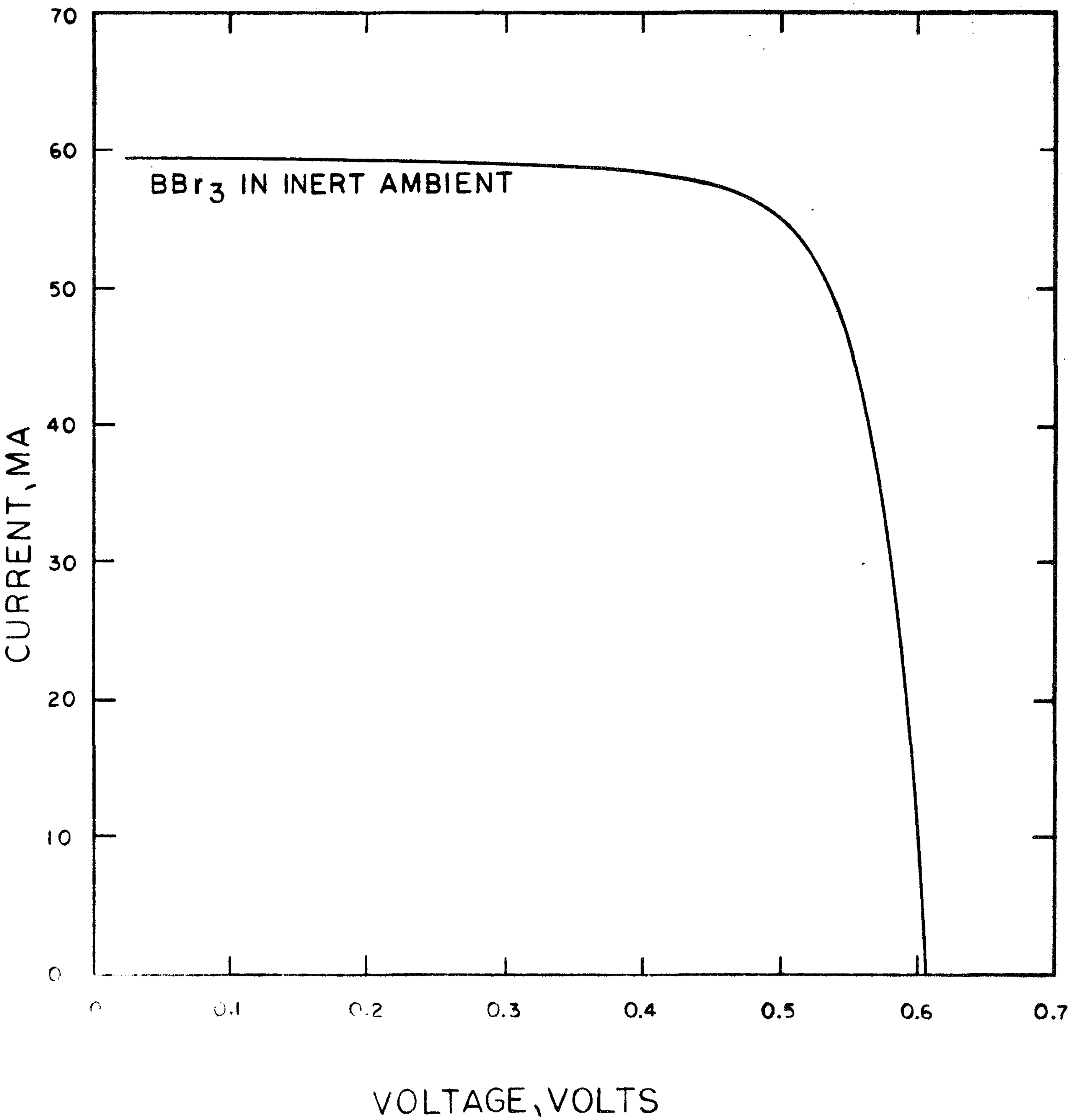

Figure 3. I-V Characteristic of 10 Minute Diffusion Using BBr_3 in an Inert Ambient. Tungsten light source - 100 mW/cm^2.

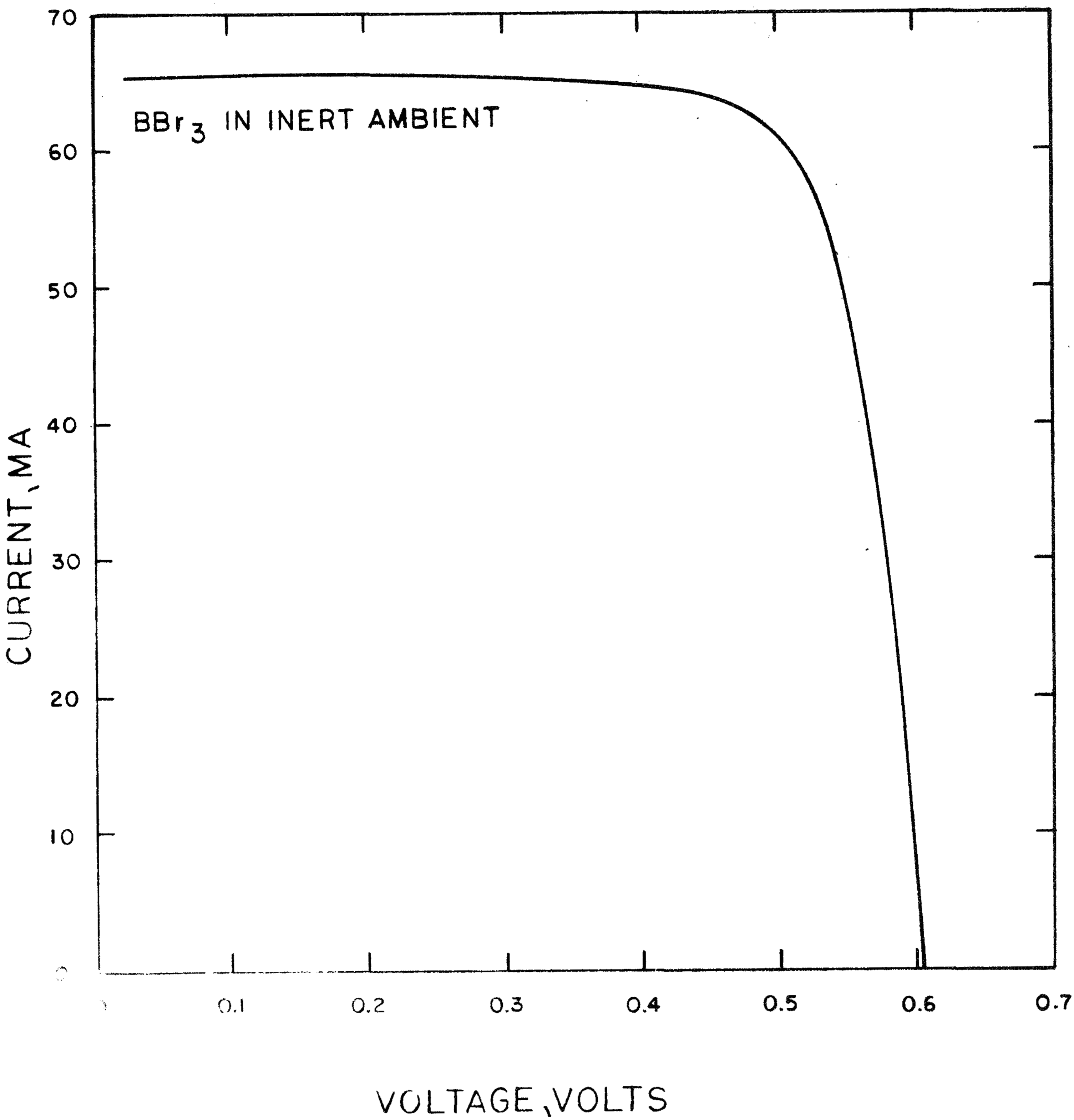

Figure 4. I-V Characteristic of 10 Minute Diffusion Using BBr_3 in an Inert Ambient. AMO simulator - 140 mW/cm^2.

curve of the same cell tested under AMO conditions (140 mW/cm^2) and the efficiency was over 11%. This indicates that a high efficiency solar cell can be made from this boron source which appears to leave the silicon blanks stress-free.

Further work on process optimization and lithium cell fabrication is needed; then it would be desirable to submit some cells of this type to the radiation test program to check for unusual recovery characteristics.

With the achievement of the good P/N cell I-V characteristic of Figure 4 from diffusion with BBr_3 in an inert atmosphere, a major milestone has been completed.

2.2 EFFECTS OF LITHIUM COVERAGE

It has been suggested that the percentage of the back surface which is covered with lithium should have an effect upon the radiation recovery characteristics of lithium cells. Cells fabricated by Heliotek have generally been painted with lithium so that the lithium source is always within .010-.020 inch of the cell edge. This undiffused region around the perimeter of the cell although small could result in residual radiation damage. Lithium would not be present in this region to anneal damage sites and the junction edge effects might degrade the characteristic curve. An experiment was designed to evaluate the effect of varying the area of this region and the significance of this residual damage. Lithium was painted on the cells as follows: the first group had 100% lithium coverage; the second, ≈85%; and the third, ≈50%. Both boron diffused slices and undiffused silicon blanks were lithium diffused; the boron diffused slices were fabricated into cells to evaluate the electrical characteristics and the blanks were used for concentration profile analysis. The undiffused regions did not affect V/I's (a measure of the slice resistivity). Also, no clear correlation could be drawn between lithium coverage and electrical output. The cells from this experiment will be delivered to JPL for radiation testing. These radiation tests should indicate whether or not complete lithium coverage of the back cell surface is important.

2.3 EIGHT-HOUR LOW-TEMPERATURE LITHIUM DIFFUSIONS

Eight hour lithium diffusions at 325°C were investigated during this quarter. In the initial diffusions there were unusually wide variations in the electrical characteristics. The range in $^V/I$'s (a measure of the slice resistivity) was much wider than that normally obtained with shorter diffusions at higher temperatures. It was also observed in these preliminary experiments that the $^V/I$'s were affected by the thickness of the lithium layer. This was also abnormal since earlier short time diffusion studies on the previous lithium cell contract had shown that decreasing the thickness of the lithium layer in order to reduce the pitting of the silicon did not change the $^V/I$'s or the lithium concentration profile.

In more recent experiments the eight hour diffusions were improved and the $^V/I$'s were under much better control, although they still seem to be less uniform than $^V/I$'s of cells from conventional lithium diffusions made at higher temperatures. Two lithium concentration profiles characteristic of the range of values typically obtained for an eight hour diffusion at 325°C are shown in Figure 5. The concentration profiles were measured by the sucessive lapping technique described in the previous contract. Curve A represents cells with $^V/I$'s ranging from ≈.55 to 1.0 ohms and Curve B represents cells with $^V/I$'s ranging from ≈1.0 to 1.3 ohms. Comparison of this eight hour diffusion to other lithium diffusions showed that the $^V/I$'s of .55 to 1.0 ohms are in the same range as those from a 90 minute diffusion with 60 minutes redistribution at 425°C and the $^V/I$'s from ≈1.0 to 1.3 ohms are in the same range as those from a 90 minute diffusion with 120 minutes redistribution at 425 °C. Figures 6 and 7 compare the lithium concentration

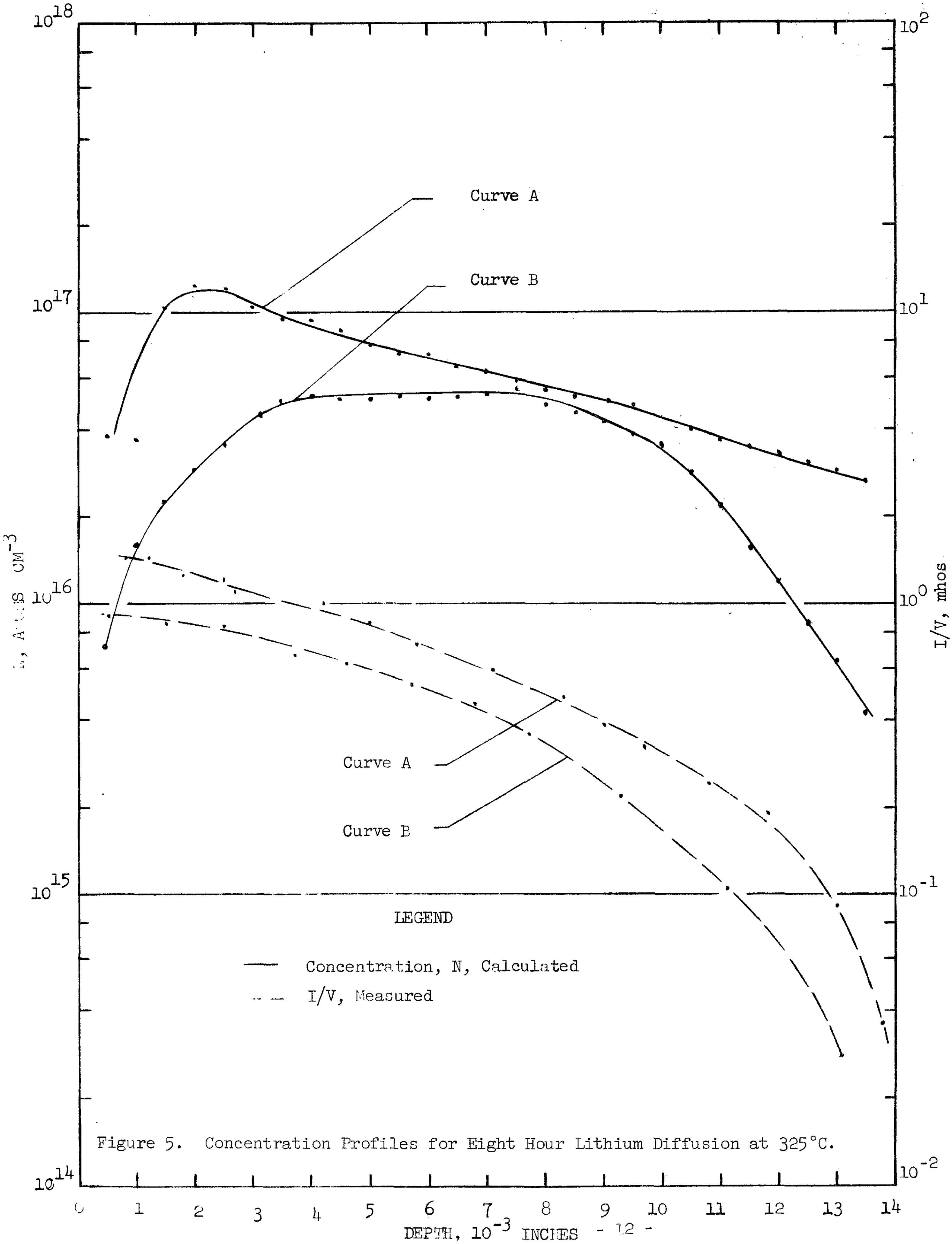

Figure 5. Concentration Profiles for Eight Hour Lithium Diffusion at 325°C.

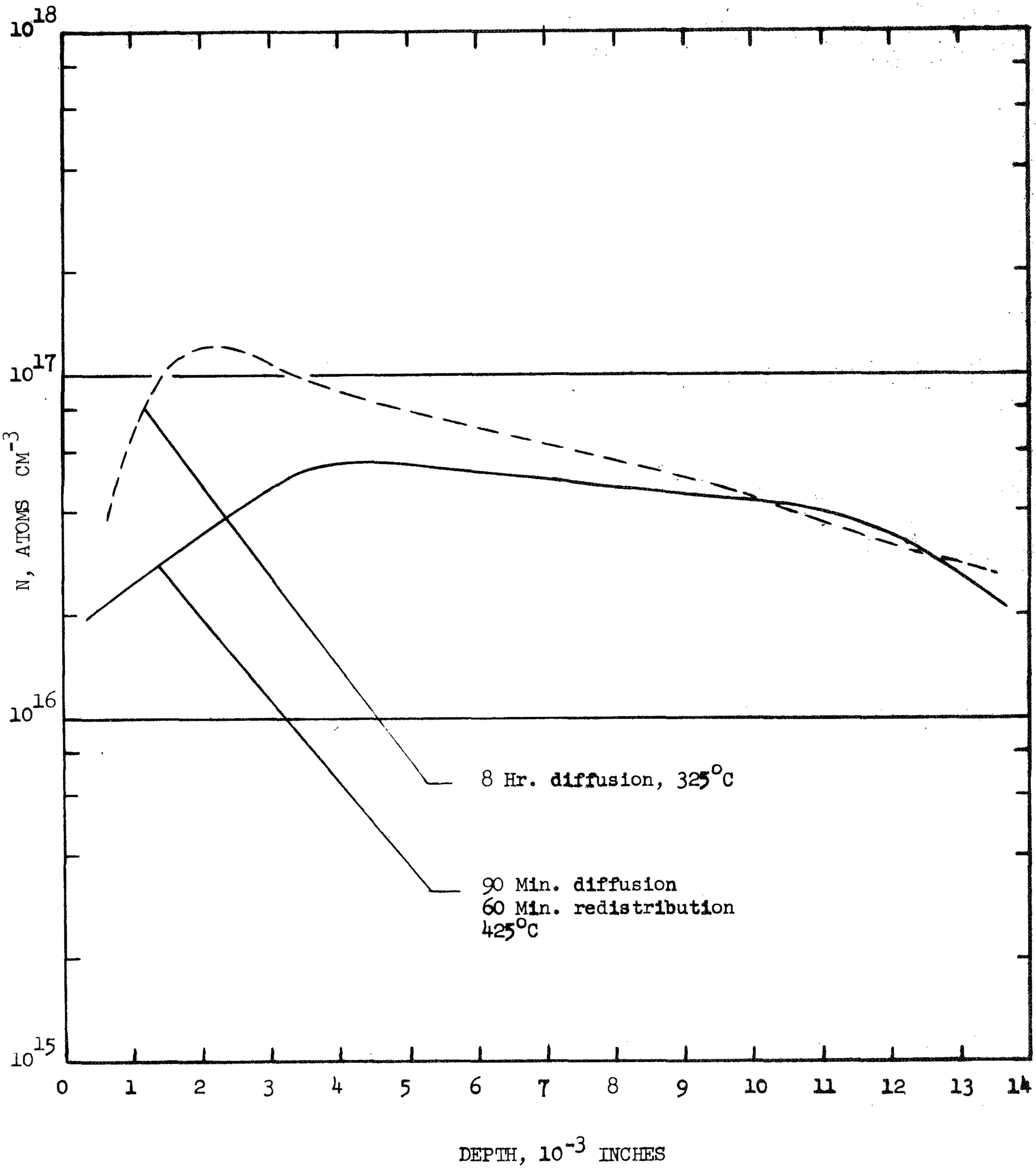

Figure 6. Comparison of Lithium Concentration Profiles.

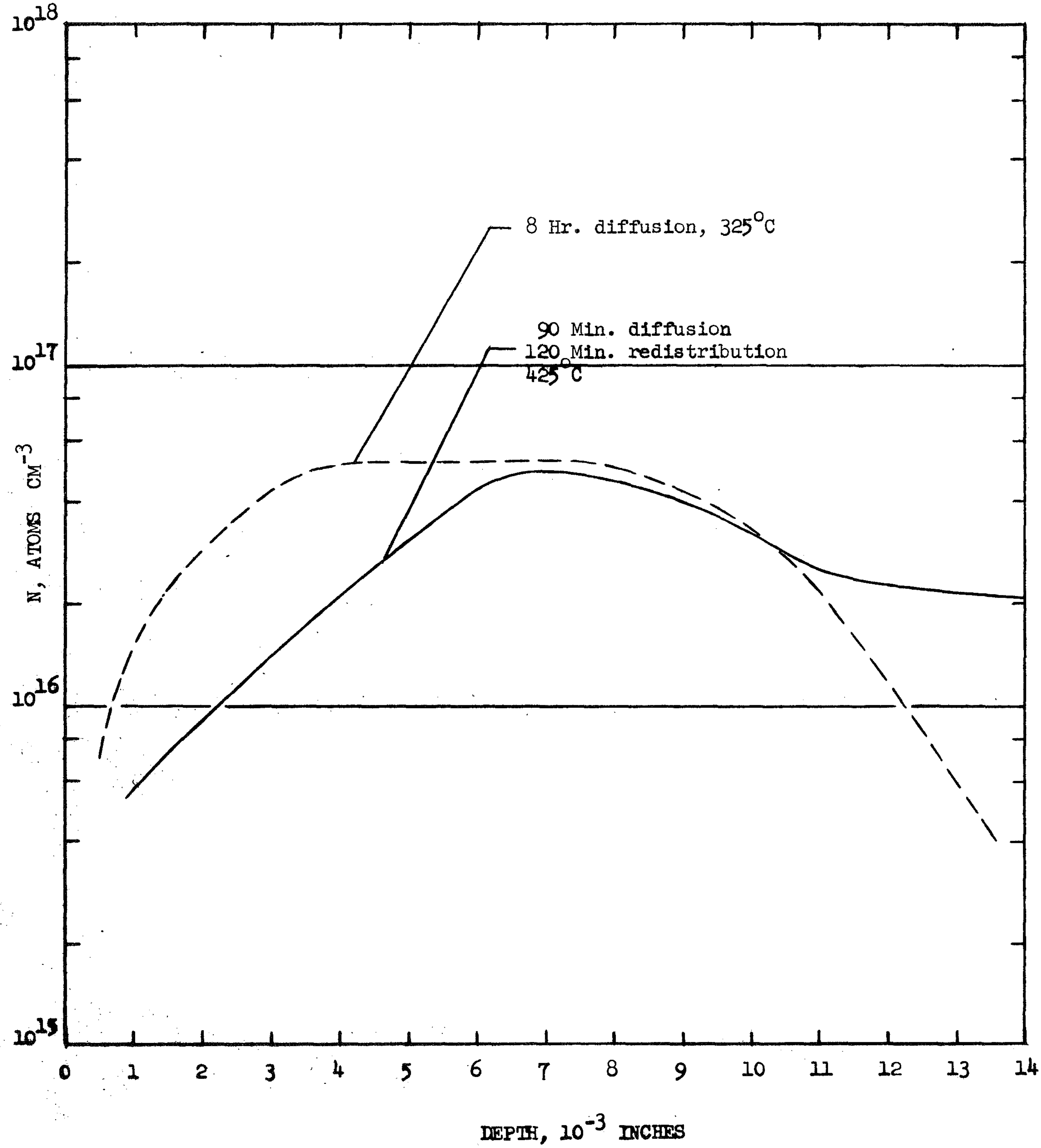

Figure 7. Comparison of Lithium Concentration Profiles.

profiles for these two 425°C diffusions with the lithium concentration profiles for the eight hour diffusion at 325°C. Figure 6 shows that the lithium concentration profile for the commonly used 90 minute 425°C diffusion with 60 minutes redistribution is considerably lower in the first .004" of silicon; however, at a depth of .008" the lithium concentrations for both diffusions are approximately the same. The eight hour (at 325°C) diffusion profile (Curve B from Figure 1) shown in Figure 7 has a higher lithium concentration at the front and a lower lithium concentration at the back than the profile for the 90 minute diffusion with 120 minutes redistribution at 425°C.

The electrical output of some of these experimental cells diffused eight hours at 325°C was exceptionally good.

Since the results were encouraging and the techniques seemed under control, JPL requested that a Lot of 60 cells be delivered for radiation studies. The data on the output of the cells for Lot 3 which were diffused eight hours at 325°C is presented in Section 2.5.

2.4 EVALUATION OF TI-AG CONTACTS

During this quarter solderless Ti-Ag contacts, which are presently used on P/N lithium cells, were evaluated. The contacts were tested by performing wire pull tests and by subjecting the cells to humidity testing in 95% relative humidity at 65°C.

Pull tests (i.e., wires soldered to the contact and pulled perpendicular to the cell surface until failure) were performed to determine the mechanical strength of the contacts. Table 1 shows the data obtained. No average pull strength of the contact can be calculated because the majority of the cells had failures in the silicon. Eighty-one percent of the failures were due to fractured silicon, rather than failing

TABLE 1

Pull Test - P/N Lithium Cells with Ti-Ag Contacts

Cell No.	Front Grams Pulled	Back Grams Pulled
6988	350 - Si Fractured	400 - Si Fractured
6976	150 - Si Fractured	1000
6986	700	1000
7081	500 - Si Fractured	450 - Si Fractured
6997	300 - Si Fractured	350 - Si Fractured
7091	600	750
7045	250 - Si Fractured	1000
7071	950	1000
7044	100 - Si Fractured	1000
7075	550	900
7035	700 - Si Fractured	500 - Si Fractured
6980	1000	550 - Si Fractured
6998A	700 - Si Fractured	600 - Si Fractured
6998B	700 - Si Fractured	425 - Si Fractured
6983	900 - Si Fractured	---

contacts, and fractures at less than 500 grams accounted for fifty percent of the silicon fractures. However, in all cases where the silicon fractures or divots did not occur, pull strengths of greater than 500 grams were obtained. It is unusual for conventional N/P cells to have silicon divots occur at these low values, so these results give a further indication of the stresses present in P/N lithium cells. This stress is presumed to be primarily due to the boron diffusion since the P/N cells with no lithium which were pull tested also failed with silicon fractures generally at less than 500 grams.

Both I-V curves and tape peel tests were used to evaluate the humidity effects on solderless Ti-Ag contacts on P/N lithium cells. The results of the tape peel tests are shown in Figure 8. After 48 hours exposure to 95% relative humidity at 65°C there was either no peeling or if peeling had occurred it was restricted to less than 5% of the contact area. After ≈100 hours exposure, an average of 35% of the front contact peeled and some edge peeling occurred at the back contact. After approximately 200 hours exposure, the front contact peeled 100% and an average of 15% of the back contact peeled. P/N cells without lithium exhibited similar results. The electrical measurements (performed in a 100 mW/cm^2 tungsten light source) showed that even after 200 hours of exposure to humidity the maximum degradation in open circuit voltage and short circuit current for any cell was 2.1%; the average I_{sc} and V_{oc} losses for all cells were 1.3% and .83%, respectively. The most significant loss factor was near maximum power due to an increase in series resistance and the subsequent rounding out of the knee. No electrical degradation was measurable after 48 hours; however, the average maximum power degradation after ≈100 and 200 hours was 4% and 5%, respectively. Table 2 shows the changes in maximum power for both float zone and crucible grown lithium cells after 200 hours of humidity exposure.

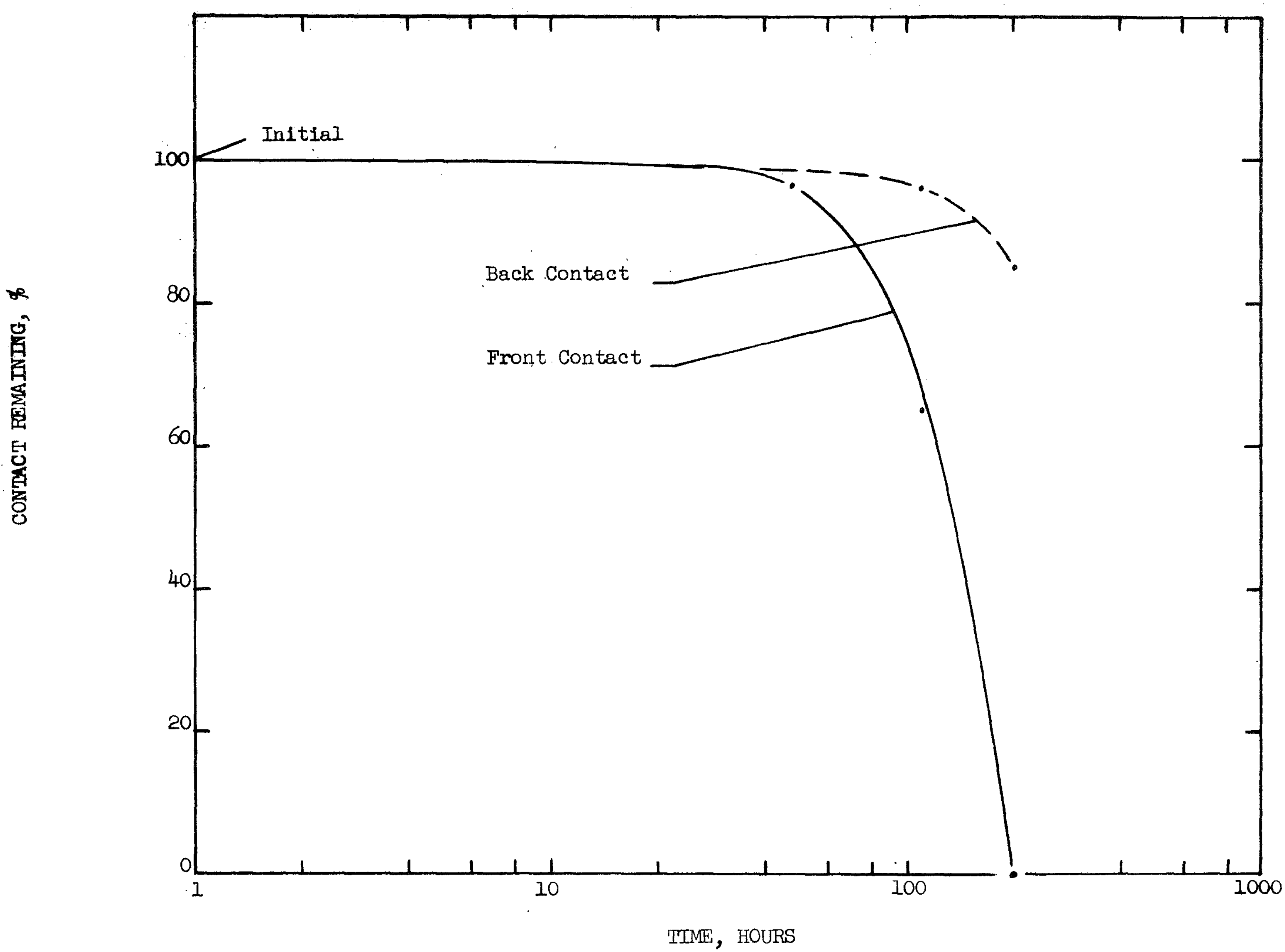

Figure 8. Effects of 95% Humidity at 65°C on Ti-Ag Contacts on P/N Lithium Cells.

TABLE 2

Effects of Humidity Exposure on the Maximum Power of P/N Lithium Cells

Cell and Type	Maximum Power: Before	After 200 Hrs.	Δ	%
Crucible Grown				
1	17.6	16.2	1.4	7.95
2	22.2	21.0	1.0	4.50
3	21.7	20.6	1.1	4.52
4	20.3	18.3	2.0	9.85
5	19.7	18.7	1.0	5.08
6	22.1	21.1	1.0	4.52
7	21.2	20.5	.7	3.30
8	21.8	21.1	.7	3.20
9	21.0	20.5	.5	2.40
10	20.6	20.0	.6	2.90
11	19.9	19.0	.9	4.50
12	19.8	19.0	.8	4.00
Float Zone				
1	17.2	16.4	.8	4.66
2	17.9	17.0	.9	5.00
3	17.2	16.6	.6	3.50
4	17.2	16.3	.9	5.20
5	18.6	17.3	1.3	7.00
6	18.3	17.5	.8	4.4

The degradation is significant, but not as great as might be expected, considering that tape peel tests after 200 hours of exposure would result in 100% peeling of the front contact. The P/N cells without lithium showed more degradation -- in some cases 24 - 45% change in maximum power occurred after 200 hours.

In summary, the Ti-Ag contact on P/N lithium cells is just as susceptible to degradation from humidity exposure as the Ti-Ag contact on standard N/P solar cells. In addition, the mechanical strength of the contacts is limited by the fracture level of boron diffused silicon slices.

2.5 CELLS FOR SHIPMENT TO JPL

The second and third shipments of 60 experimental cells each were delivered to JPL during this quarter. Lot 2 consisted of 60 cells fabricated from 100 ohm cm Lopex silicon. The cells were diffused 90 minutes and redistributed 120 minutes at 425°C. These cells showed the same variations in open current voltage which have previously been observed with Lopex silicon. Some cells with high outputs had not only high short circuit currents but also open curcuit voltages of 570 - 580 mV. Some of the lower output cells had open circuit voltages as low as 540 mV. The cause is still uncertain; it could be dependent to some degree on oxygen concentration which some investigators have indicated varies considerably in Lopex silicon. At any rate, Lopex silicon seems to be the least predictable with respect to the lithium cells fabricated from it.

Figures 9 and 10 show the short circuit current and maximum power distributions for Lot 2 cells. Eighty-seven cells were included and the average output was 25.4 mW. 10% of the cells had outputs equal to or greater than 27.6 mW and 95% had outputs ≥ 23.4 mW. With respect to the short circuit current,

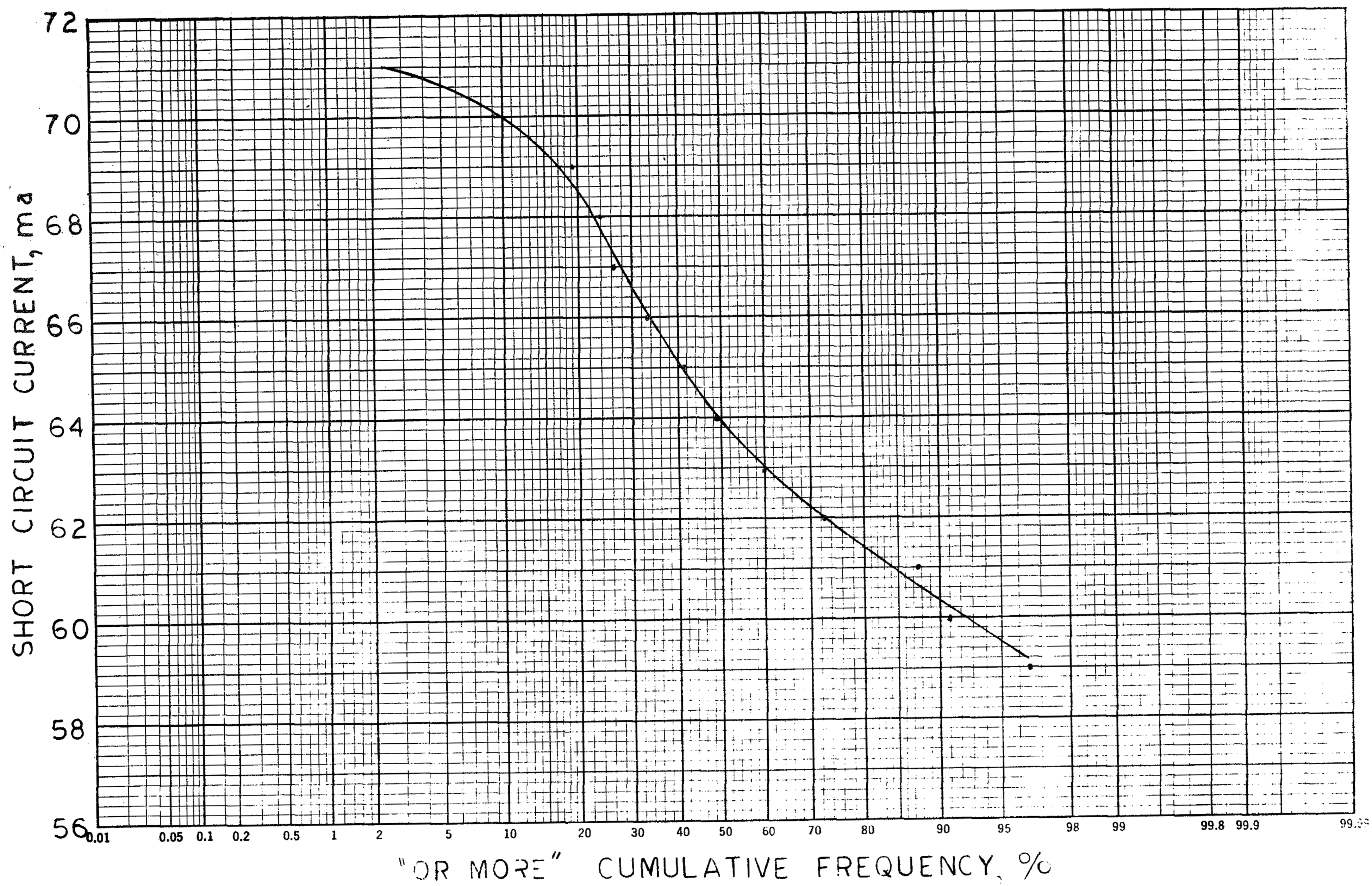

Figure 9. Short Circuit Current Distribution of Lithium Cells Fabricated for the Second Lot (87 cells). 100 ohm cm Lopex cells, lithium diffused 90 minutes and redistributed 120 minutes at 425°C: measured in solar simulator at 140 mW/cm^2.

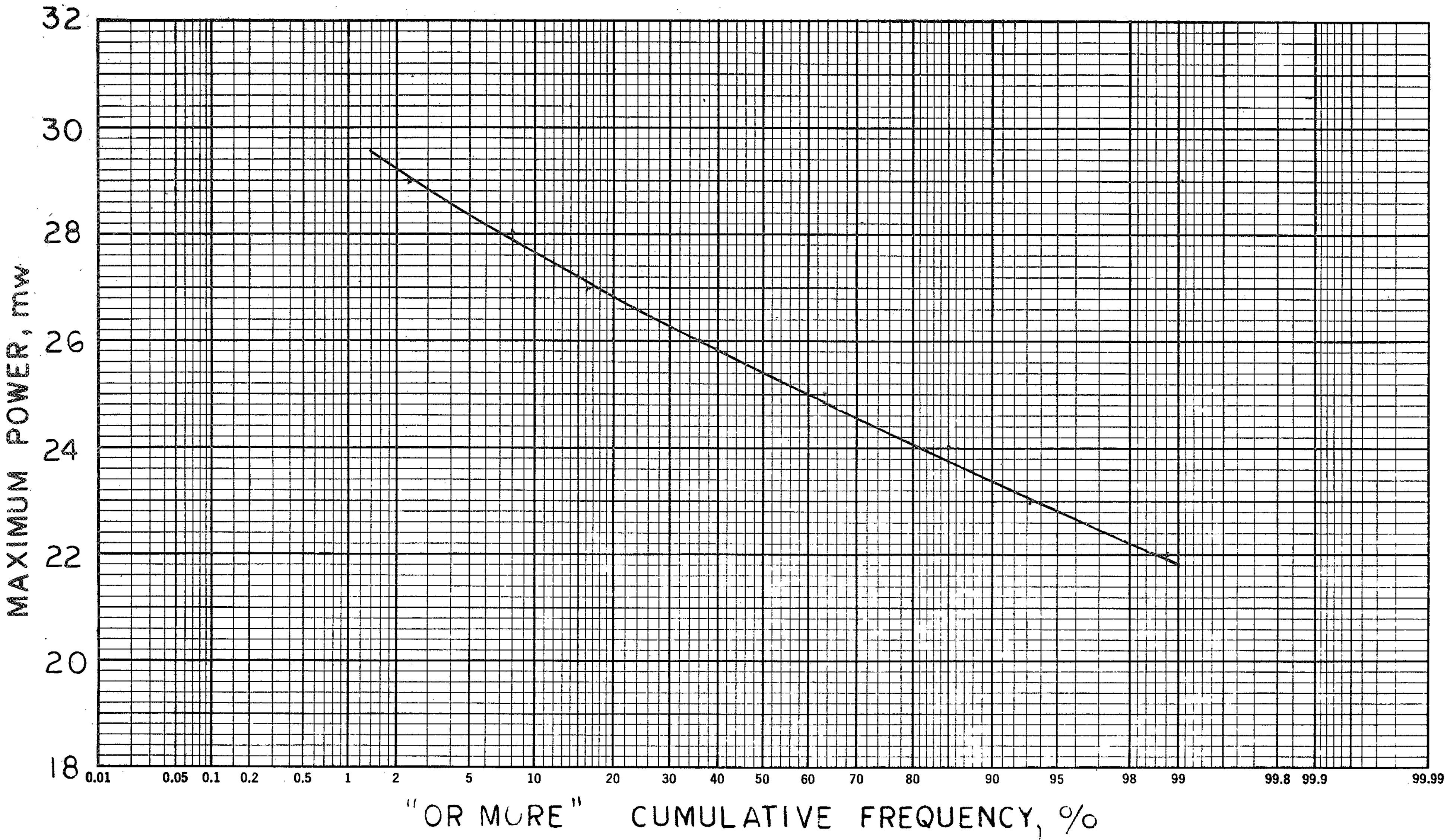

Figure 10. Maximum Power Distribution of Lithium Cells Fabricated for the Second Lot (87 cells). 100 ohm cm Lopex cells, lithium diffused 90 minutes and redistributed 120 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

10% were ≥ 70.0 mA, 90% were ≥ 60.4 mA, and the average was 64.0 mA.

Lot 3 consisted of 20 ohm cm crucible grown cells lithium diffused for eight hours at 325°C. After working with these diffusion parameters and gaining good control of the process, cells with exceptionally high short circuit currents and outputs were obtained. The statistical analyses of the short circuit current and maximum power included only the 60 cells shipped to JPL, since a number of the cells had poor I-V curve shapes due to contact shunting problems. Some of the cells with poor curve shapes exhibited a carrier removal effect in that they did not have exceptionally high dark reverse currents at .7V but did pass high current at low voltages.

The maximum power distribution of the 60 cells in Lot 3 was narrow and high (Figure 11). The average output was 30 mW, with 10% of the cells having outputs ≥ 32 mW and 90% having outputs ≥ 27 mW. The short circuit current distribution (Figure 12) was much wider with 10% of the cells ≥ 74.6 mA, 90% ≥ 62.5 mA and an average short circuit of 68.6 mA.

The tenth lot of cells fabricated during last year's lithium cell research contract resulted in the best distribution of crucible grown lithium cells. Table 3 compares the maximum power cumulative frequency distributions at 10, 50, and 90% for Lot 10 on last year's contract and Lot 3 on the present contract. The values shown are for the same intensity at AMO equivalent sunlight.

TABLE 3

Maximum Power Cumulative Frequency Distribution

	Lot 3	Lot 10
10%	32.0 mW	30.4 mW
50%	30.0 mW	28.3 mW
90%	27.0 mW	26.1 mW

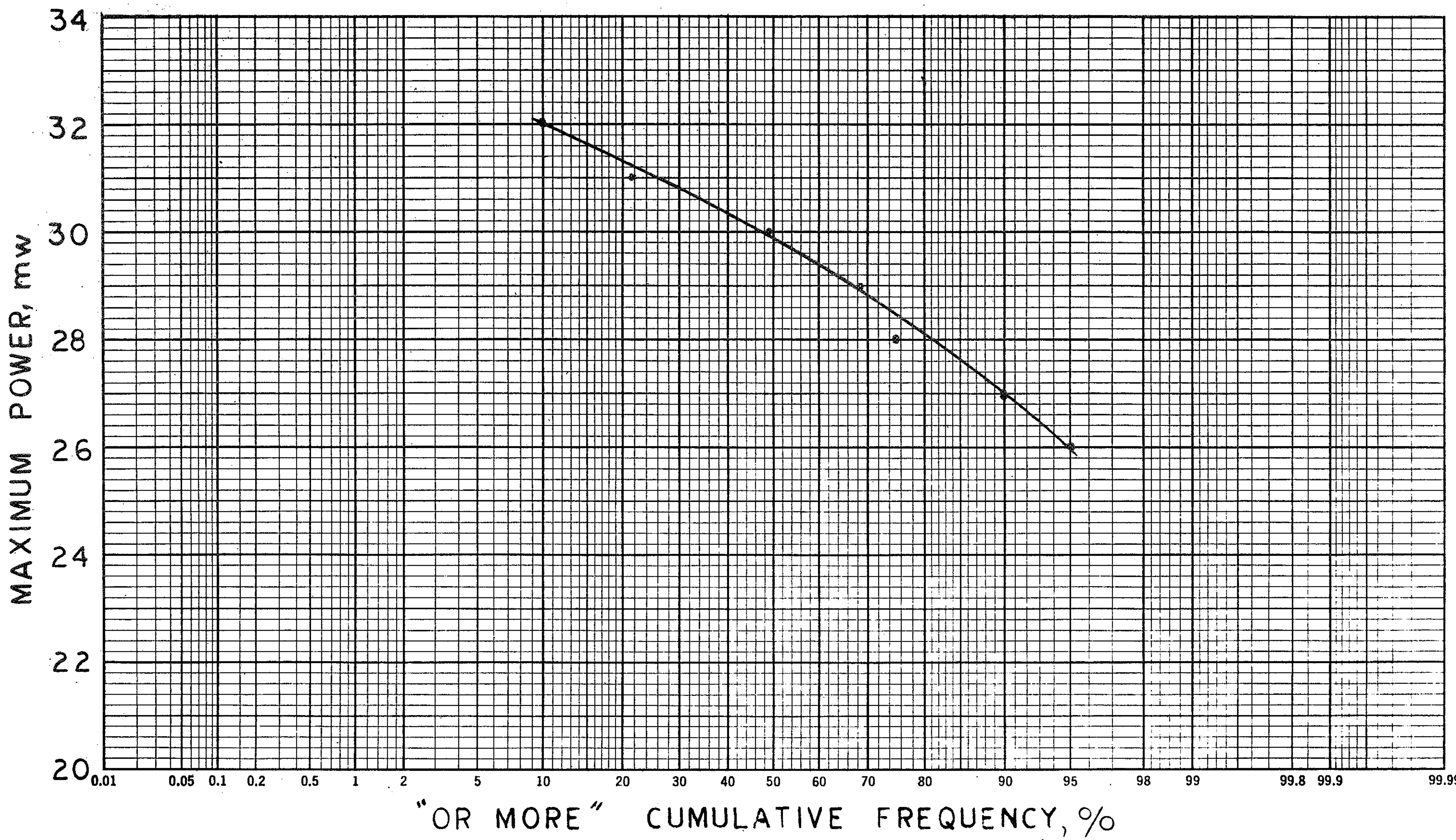

Figure 11. Maximum Power Distribution of Lithium Cells Fabricated for the Third Lot (60 cells). 20 ohm cm crucible grown cells, lithium diffused 8 hours at 325°C; measured in solar simulator at 140 mW/cm^2.

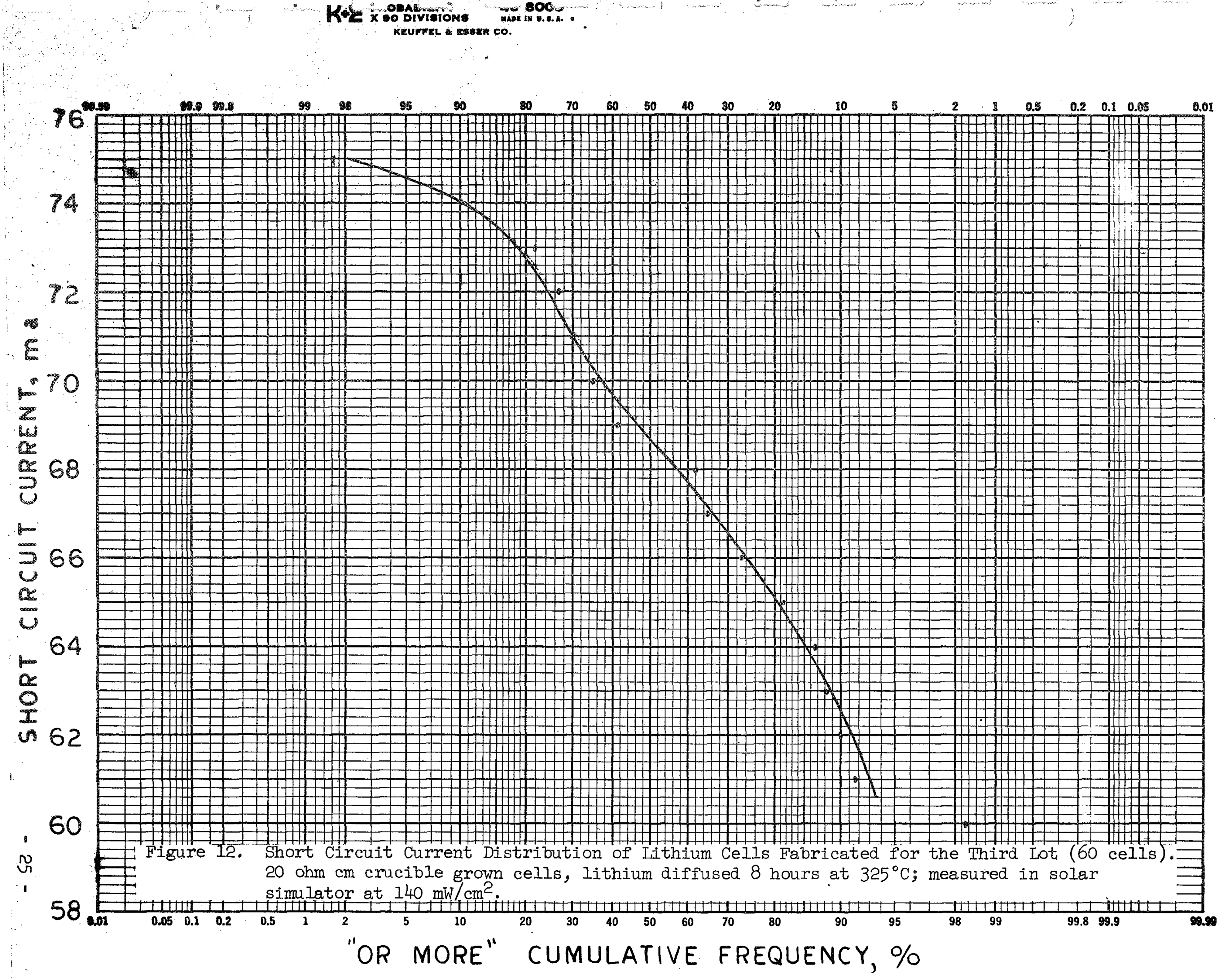

Figure 12. Short Circuit Current Distribution of Lithium Cells Fabricated for the Third Lot (60 cells). 20 ohm cm crucible grown cells, lithium diffused 8 hours at 325°C; measured in solar simulator at 140 mW/cm^2.

If the radiation recovery of these cells from Lot 3 is equivalent to previous tests, then a considerable improvement in cell efficiency can be realized with this 8 hour diffusion at 325°C.

3.0 CONCLUSIONS

Good P/N cell I-V characteristics have been achieved by diffusing with a BBr_3 source in an inert atmosphere. Continued effort in this area should result in cell efficiencies as good as or better than those obtained with the BCl_3 diffusion source. An important conclusion is that silicon stressing has been negligible with the BBr_3 diffusion. Large area lithium cells are now feasible due to the reduced stresses associated with the BBr_3 diffusion.

Variations in lithium coverage do not affect the $^V/I$'s or I-V characteristic curves; however, it is expected to have an influence on radiation recovery.

The Ti-Ag contact on P/N lithium cells is not humidity resistant and electrical degradation does occur.

The eight hour lithium diffusion at 325°C has resulted in the highest efficiency for the amount of lithium present of any cells fabricated to date. Efficiencies as high have only been observed for cells with low lithium concentrations.